

CLAIMS

1. Perfluorodiacylperoxides having the following structures:

wherein:

when R_f is F, $R_{f'}$, $R_{f''}$ are both $-CF_3$;

when R_f is -CF₃, R_f , and R_f , are C_1 - C_3 linear or branched perfluorooxyalkyl groups;

wherein:

 R_{ν} is selected from F, perfluorooxyalkyl, C_1-C_3 linear or branched perfluoroalkyl;

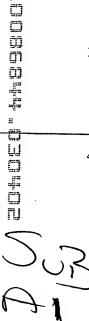
 X_1, X_2 are selected from F, perfluoroalkyl, $C_1 - C_3$ linear or branched perfluorooxyalkyl.

$$CF_2$$
 CX_3 $- C(0) - O-O- C(0) - CX_3$ CF_2 CF_2 CF_2 CF_2 CF_2 CF_2

wherein:

$$n = 1 - 3$$

 X_3 is selected from F, $C_1 \hbox{-} C_3$ linear or branched perfluoro-



alkyl, with the proviso that for n=3, X_3 cannot be F; said perfluorodiacylperoxides meet the following condition: the thermal decomposition constants K_d (sec⁻¹) in the presence of water do not undergo substantial variations with respect to the thermal decomposition constants in absence of water.

- 2. A polymerization process of one or more fluorinated monomers wherein the perfluorodiacylperoxides according to claim 1 are used as polymerization initiators.
- 3. A polymerization process according to claim 2, wherein the polymerization is carried out in aqueous medium, in suspension, in emulsion or in microemulsion.
- 4. A polymerization process according to claims 2-3, wherein at temperatures of the order of 50°-80°C, the perfluorodiacylperoxides of structure (C) or the compound of structure (A) having the formula:

are used.

5. A polymerization process according to claims 2-3, wherein at temperatures of the order of -20° - +25°C, the perfluorodiacylperoxides of structure (A) of formula:

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$$R_{f} \begin{cases} \begin{cases} R_{f}, & R_{f}, \\ C - C(0) - O - O - C(0) - C - R_{f}, \\ R_{f''} & R_{f''}, \end{cases}$$

are used, wherein when $R_{\rm f}$ is -CF3, $R_{\rm f}$ and $R_{\rm f}$ are C_1-C_3 linear or branched perfluorooxyalkyl groups.

- 6. A polymerization process according to claims 2-5, wherein the fluorinated monomers are selected from:
 - C_2 - C_8 perfluor colefins, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP);
 - C_2 - C_8 hydrogenated fluoroolefins, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene, CH₂=CH/ R_f perfluoroalkylethylene, wherein R_f is a C_1 - C_6 perfluoroalkyl, hexafluoroisobutene;
 - C_2 - C_8 chloro-fluorolefine, such as chlorotrifluoroe-thylene (CTFE);
 - CF_2 =CFOR_f (per)fluoroalkylvinylethers (PAVE), wherein R_f is a C_1 - C_6 (per)fluoroalkyl, for example CF_3 , C_2F_5 , C_3F_7 ;
 - CF_2 =CFOX (per)fluoro-oxyalkylv nylethers, wherein X is: a C_1 - C_{12} alkyl, or a C_1 - C_{12} oxyalkyl, or a C_1 - C_{12} (per)fluorooxyalkyl having one or more ether groups;
 - perfluorodioxoles, such as 2,2,4trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), 2,2bis-trifluoromethyl-4,5-difluoro-dioxole (PPD);

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- sulphonic monomers, such as CF₂=CFOCF₂CF₂SO₂F;
- fluorinated dienes such as $CF_2=CFOCF_2CF_2CF=CF_2$, $CF_2=CFOCCl_2CF=CF_2$, $CF_2=CFOCCl_2CF=CF_2$, $CF_2=CFOCCl_2CF=CF_2$, $CF_2=CFOC(CF_3)_2OCF=CF_2$.
- 7. A polymerization process according to claims 2-6, wherein the perfluorodiacylperoxide initiator is fed in a continuous way or by a single addition at the starting of the polymerization.
- 8. A polymerization process according to claims 2-7, wherein the amount of perfluorodiacy peroxide initiator is in the range 0.0001%-5% by moles with respect to the amount of the fed monomers.

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